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(54) **Oxide superconducting wire, manufacturing method thereof, oxide superconducting coil and cable conductor**

Draht aus supraleitendem Oxid, Verfahren zur Herstellung, Spule und Kabel aus supraleitendem Oxid
Fil en oxyde supraconducteur, procédé de sa fabrication, bobine et câble en oxyde supraconducteur

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(56) References cited:

EP-A- 0 377 294	EP-A- 0 503 525
WO-A-89/02656	FR-A- 2 119 205
FR-A- 2 309 986	US-A- 3 829 964
US-A- 3 835 242	

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- **PATENT ABSTRACTS OF JAPAN vol. 016 no. 441 (E-1264) ,14 September 1992 & JP-A-04 155711 (CENTRAL RES INST OF ELECTRIC POWER IND) 28 May 1992,**
- **S.JIN ET AL.: "High Tc superconductors - composite wire fabrication", APPL. PHYS. LETT., USA, 20. July 1987, vol. 51, no. 3, pages 203 to 204**

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Description**BACKGROUND OF THE INVENTION****5 Field of the Invention**

[0001] The present invention relates to a superconducting wire and manufacturing method thereof, as well as to an oxide superconducting coil and a cable conductor. More specifically, the present invention relates to an oxide superconducting wire, manufacturing method thereof, an oxide superconducting coil and a cable conductor having high critical current density and low a.c. loss.

Description of the Background Art

[0002] In recent years, superconducting materials of ceramics, i.e., oxide superconducting materials, are watched with interest due to higher critical temperatures thereof. Among these materials, yttrium, bismuth and thallium oxide superconducting materials which exhibit high critical temperatures of about 90K, 110K and 120K respectively, are expected for practical application.

[0003] A single-filamentary oxide superconducting wire having high critical current density formed of such oxide superconducting materials is obtained by heat treating and then covering with a metal sheath the material powder, drawing, rolling and by further heat treatment. Similarly, an oxide superconducting multi-filamentary wire having high critical current density is obtained by heat treating powder mainly consisting of oxide superconducting material, then covering the same with a metal sheath, drawing and putting together the as-obtained wires to provide a multi-filamentary wire, and further by drawing, rolling and heat treating the same.

[0004] It has been conventionally known that an oxide superconducting wire having higher critical current density can be obtained by repeating several times the steps of rolling and heat treatment in manufacturing such an oxide superconducting wire.

[0005] If such an oxide superconducting wire is to be applied to an a.c. cable or magnet, it must have low a.c. loss, high strength and superior property under bending-strain, in addition to the high critical current.

[0006] The single-filamentary and the multi-filamentary oxide superconducting wires manufactured through the conventional method described above have as high a critical density as 30000A/cm² or higher.

[0007] However when an a.c. current is applied with the wire wound in a coil, there is generated an a.c. loss heat radiation. This is because an induced current flows between the metal sheath and the ceramics when an a.c. current is applied, resulting in heat radiation caused by a.c. loss of normal conduction resistance of the metal sheath, as compared to the case when a d.c. current is applied, in which case current flows only through the ceramic portions. Since the temperature of the coil as a whole increases, critical current density is decreased.

[0008] Accordingly, the operational frequency of the coil manufactured in accordance with the conventional method has been about 0.1Hz at the highest. Document EP-A-0 503 525 relates to a method for manufacturing superconductive wires in which first metal sheaths of circular cross section are filled with a superconductive material. The first metal sheaths consist of silver and/or a nickel copper compound or another suitable material. The filled first sheaths are drawn. Afterwards a plurality of these drawn first sheaths is inserted in a second metal sheath of nickel copper compound or of another suitable metal alloy and finally twisted. In this wire disconnection is sometimes caused due to inferior tensile strength and bending stress. Furthermore, if CuNi alloy and silver are used for the first metal sheath, it is important to note that CuNi alloy is significantly degraded by oxidation at higher temperatures in air.

[0009] The document Appl.Phys.Lett., Vol.51, No.3, 20 July 1987, pages 203-204; S.Jin et al.: "High T_c superconductors - composite wire fabrication" relates to high T_c superconductors-composite wire fabrication. In this method a superconductive powder is introduced into a normal metal tube. This normal metal tube comprises Ag alone or Cu with a Ni/Au diffusion barrier. The filled normal metal tube is drawn, bundled, placed inside a normal metal tube and further drawn to produce a multifilamentary composite configuration. Proper diffusion barrier metals are Ag and Au wherein Ag is a very attractive metal component. The resistance against electromagnetic stress, when wound into a coil and current is applied, and the strength of the subject matter of this are not very high. Furthermore, there is a remarkable a.c. loss related to the frequency.

[0010] Document WO89/02656 relates to a sheathing material for superconducting wires, which is a silver alloy having a melting temperature higher than that of pure silver. With such a sheathing material a single layer wire can be provided which melts only at a temperature above the optimal temperature for recovery by annealing so that the original superconductivity can be restored or improved after deforming.

Summary of the invention

[0011] The object of the present invention is to solve the above problems and to provide a method of manufacturing an oxide superconducting wire and a tape-like oxide superconducting wire obtainable by such a method, wherein this wire has high operational frequency, high strength as well as superior property under bending strain and can be used for a coil or a cable.

[0012] This objects is solved by a method according to claim 1 and by an oxide superconducting wire according to claim 6.

[0013] Further embodiments are disclosed in the subclaims.

[0014] The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention when taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] Figs. 1 to 3 show steps of manufacturing an oxide superconducting wire in accordance with the background of the present invention.

[0016] Fig. 4 is a perspective view showing the oxide superconducting wire of one example of the background of the present invention.

[0017] Fig. 5 is a cross section schematically showing the structure of the oxide superconducting wire shown in Fig. 4.

[0018] Fig. 6 is a cross section schematically showing the structure of the oxide superconducting wire of an example of the present invention.

[0019] Fig. 7 is a perspective view showing an oxide superconducting multi-filamentary wire of an example of the present invention.

[0020] Fig. 8 is a perspective view showing a conventional oxide superconducting multi-filamentary wire.

[0021] Fig. 9 illustrates the angle of inclination of the superconducting wire in the present invention.

[0022] Fig. 10 shows a structure of an apparatus for measuring the a.c. loss of the oxide superconducting wire.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0023] According to the background of the present invention, an oxide superconducting wire is provided, which wire is a tape-like oxide superconducting wire including a plurality of filaments of oxide superconductor embedded in a matrix, with the filament twisted spirally along the longitudinal direction of the tape wire.

[0024] As mentioned above, the filament of oxide superconductor embedded in the matrix is twisted spirally along the longitudinal direction of the wire. Therefore, the induced current flowing between the matrix and the filament is cut at every twist pitch and flows in a small loop, so that the magnitude of the current is limited. As a result, heat radiation caused by a.c. loss of the matrix can be avoided. This function will be discussed in detail with reference to the figures.

[0025] Fig. 8 is a perspective view showing a conventional oxide superconducting multi-filamentary wire.

[0026] Referring to Fig. 8, the multi-filamentary wire is constituted by filaments 11a, 11b, 11c and 11d of oxide superconductor embedded in a silver matrix 2.

[0027] When the multi-filamentary wire structured in this manner experiences a change in the magnetic field dB/dt generated, for example, by a coil, there is generated a large induced current loop 13 other than the applied current between filaments 11a and 11b because of an induced electromotive force, and therefore a large loop current I flows. Accordingly, heat radiation derived from the superconducting resistance of silver matrix 2 increases in proportion to $(dB/dt)^2$ with the frequency.

[0028] By contrast, Fig. 7 is a perspective view showing an oxide superconducting multi-filamentary wire of one example for the background of the present invention.

[0029] Referring to Fig. 7, the multi-core wire is constituted by filaments 1a, 1b, 1c and 1d of oxide superconductor embedded in silver matrix 2, with each of the filaments 1a, 1b, 1c and 1d twisted spirally along the longitudinal direction of the multi-filamentary wire.

[0030] When the multi-filamentary wire structured in this manner experiences the change in the magnetic field dB/dt , the induced current loop 3 is limited by the length L_p of the twist pitch of the filaments 1a and 1b. Consequently, the magnitude of loop current I_p also decreases, and the a.c. loss decreases as the length L_p of the twist pitch decreases.

[0031] Preferably, the pitch of the twist should be at least the width of the wire. This prevents disconnection of the wire during twisting, rolling and drawing.

[0032] Preferably, the matrix may be silver or silver alloy, since the matrix of silver or silver alloy can serve as a stabilizer. The a.c. loss mentioned above is in reverse proportion to the resistance value of the matrix. In order to reduce the a.c. loss, it is preferable to provide a matrix having high resistance, by using silver alloy.

- [0033] According to another aspect relating to the present invention, an oxide superconducting wire is provided which is similar to the wire of the aforementioned aspect and additionally characterized in that each of the plurality of filaments is covered by silver or silver alloy, and a barrier layer of metal or metal alloy having the resistance value at a room temperature higher than that of silver alloy and in the range of 10^{-6} to $10^{-10}\Omega\text{m}$ is provided to surround one or more filaments covered by silver or silver alloy in the longitudinal direction of the wire.
- 5 [0034] More preferably, the barrier layer should be formed of metal or metal alloy having the resistance value at a room temperature in the range of from 10^{-7} to $10^{-9}\Omega\text{m}$.
- 10 [0035] As described above, according to the present invention, a barrier layer of high resistance is provided to surround the filament in the longitudinal direction of the wire is provided. The barrier layer may be provided thin over the surface or at the interface between the oxide superconducting material and the metal sheath before the single-filamentary wires are put together, and as it experiences work hardening during the subsequent steps of drawing, twisting and rolling, disconnection is not caused. In addition, since the barrier material experiences appropriate work hardening, tensile strength and bending strength of the finished tape are improved, and therefore an oxide superconducting wire, which has high strength and high resistance against high electromagnetic stress when it is wound into a coil and current is applied, can be obtained.
- 15 [0036] According to the background of the present invention, an oxide superconducting coil is provided which is formed of a tape-like oxide superconducting wire including a plurality of filaments of oxide superconductor embedded in a matrix, with each filament twisted spirally along the longitudinal direction of the tape wire. In the superconducting wire structured in this manner, heat radiation caused by the a.c. loss of the matrix is reduced as already described. Therefore, a coil having high operational frequency can be obtained.
- 20 [0037] In accordance with the background of the present invention, an oxide superconducting cable conductor is provided, which is formed of a tape-like oxide superconducting wire including a plurality of filaments of oxide superconductor embedded in a matrix, with each filament being twisted spirally along the longitudinal direction of the tape wire. In the superconductor wire structured in this manner, heat radiation caused by a.c. loss of the matrix is reduced as already described. Therefore, a cable conductor having high operational frequency can be obtained.
- 25 [0038] According to the background of the present invention, a method of manufacturing an oxide superconducting wire is provided which includes the steps of heat treating and then covering with a metal sheath, powder mainly consisting of oxide superconducting material, drawing and putting together the as-obtained wires to provide a multi-filamentary wire, drawing and rolling, and heat treating, in which in the step of drawing and rolling after the wires are put together to provide a multi-filamentary wire, each as-obtained wire with circular cross section is drawn, twisted and then rolled.
- 30 [0039] According to this method, by this twisting, the induced current flowing between the metal sheath and the ceramics is cut at every pitch of the twist and flows in a small loop, so that the magnitude of the current is limited and heat radiation caused by the a.c. loss of the metal sheath can be avoided. Therefore, operational frequency when the wire is applied to a coil or a cable in the conventional manner can be increased. The twisting is effected after the material powder is covered by the metal sheath, drawn, put together to provide a multi-filamentary wire and again drawn, before rolling. Therefore, there is not an irregularity of filaments inside after rolling, and therefore, rolling can be carried out easily.
- 35 [0040] A technique for reducing surface of a shielded current loop by twisting filaments in a metal superconducting wire having circular cross section has been disclosed in Yamamura et al. Chodendo Kogaku (Superconductivity Engineering) 1974, pp. 64-66.
- 40 [0041] However, a background of the present invention is directed to a very thin tape-like oxide superconducting wire. According to this background, it becomes possible to twist the filaments in the tape-like wire by twisting the wire while it has circular cross section and then rolling.
- 45 [0042] Preferably, after the wires are twisted, the wires should be again drawn and rolled.
- [0043] Since the wires are drawn, then twisted and again drawn, swells of the wires generated during the twisting process can be eliminated. Therefore, after rolling, there is not snaking of the tape, and the tape can be uniformly rolled. There is not a possibility of untwisting of the filaments in the tape.
- 50 [0044] Preferably, the pitch of the twist after rolling should be made at least the width of the wire after rolling. If the twist pitch is made equal to or larger than the tape width after rolling, the wire is not disconnected during the steps of twisting, rolling and drawing.
- 55 [0045] More preferably, the angle of inclination at the step of twisting after rolling should be made at least 0.5° with respect to the direction of the wire. If the twisting is effected in this range, the filament simply has its arrangement directly changed in the longitudinal direction, and therefore uneven processing of the filament is prevented. Further, since the filament is arranged at an angle with respect to the longitudinal direction of the tape because of the twist, the bending-strain of the filament when the tape is bent can be reduced as a result. Therefore, property under stain of the tape with respect to the critical current can be improved when the tape is twisted. If the angle of twist is smaller than 0.5° , the effect of twisting is not obtained, and this effect can be obtained if the angle is 0.5° or larger.

[0046] The angle of inclination here refers to the maximum angle α of the filament 51 positioned at the outermost layer of the wire and the center line 50 along the longitudinal direction of the wire.

[0047] According to the present invention, a method of manufacturing an oxide superconducting wire is provided which includes the steps of heat treating and then covering with a metal sheath, powder mainly consisting of an oxide superconducting material, drawing and putting together the as-obtained wires to provide a multi-filamentary wire, drawing and rolling, and heat treating, in which a metal or metal alloy having resistance value at a room temperature higher than that of the metal sheath and in the range of 10^{-6} to $10^{-10} \Omega\text{m}$ is provided at the surface of the as-obtained single filamentary wire or between the oxide superconducting material and the metal sheath, before the single filamentary wires are put together to provide the multi-filamentary wire.

[0048] More preferably, the metal or metal alloy deposited at the surface of the single-filamentary wire or at the interface between the oxide superconducting material and the metal sheath has a resistance value at a room temperature in the range of 10^{-7} to $10^{-9} \Omega\text{m}$.

[0049] In this manner, a barrier layer of metal or metal alloy having high resistance is provided at the surface of the single-filamentary wire or at the interface between the oxide superconducting material and the metal sheath. The barrier of high resistance disposed between the filaments may be provided thin over the surface or at the interface between the oxide superconducting material and the metal sheath before the single-filamentary wires are put together. Since the barrier experiences work hardening during the subsequent steps of drawing, twisting and rolling, disconnection is not caused. Further, since the barrier material experiences appropriate work hardening, tensile strength and bending strength of the finished tape are improved, and therefore an oxide superconducting wire which has high strength and high resistance against high electromagnetic stress when it is wound into a coil and current is applied thereto, can be obtained.

[0050] Preferably, in the steps of drawing and rolling after the wires are put together to provide a multi-filamentary wire, the as-obtained wire having the circular cross section is drawn and twisted. By twisting the wire in this manner, the heat radiation caused by the a.c. loss of the metal sheath can be avoided, as already described.

[0051] As described above, according to the present invention, an oxide superconducting wire with low a.c. loss can be obtained. Therefore, the oxide superconducting wire manufactured in accordance with the present invention can be applied to an oxide superconducting magnet or cable operated at a high frequency including power frequency of 0.1Hz or higher, and it can be also applied widely to various coils for a.c. motors such as induction motors, synchronous motors, as well as for transformers, and to large-capacity a.c. cable conductors.

[0052] Further, according to the present invention, an oxide superconducting wire which has not only the low a.c. loss but also high strength and superior property under strain can be obtained.

[0053] It is difficult to reduce the twist pitch in actual manufacturing. However, when silver alloy is used, similar characteristic effect as obtained when the twist pitch is reduced, can be obtained.

[0054] The foregoing and other objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of the present invention.

[0055] The oxide superconducting wire, superconducting coil and manufacturing method thereof in accordance with the present invention will be described.

(Example 1 illustrating the background of the present invention)

[0056] Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO were mixed to have the composition ratio of $\text{Bi:Pb:Sr:Ca:Cu}=1.81:0.40:1.98:2.21:3.03$. The mixed powder was successively subjected to heat treatments in the ambient atmosphere at 750°C for 12 hours, 800°C for 8 hours, and in a reduced pressure atmosphere of $133,32 \text{ Pa}$ (1Torr), at 760°C for 8 hours. After each step of heat treatment, the powder was pulverized. The powder obtained through the heat treatment and pulverization was further pulverized by a ball mill, and powder of sub micron order was obtained. The powder was subjected to heat treatment at 800°C for 2 hours, and filled in a metal pipe having the outer diameter of 12mm and inner diameter of 9mm.

[0057] The powder filled in the silver pipe was drawn to 1mm and thus a strand was fabricated. Thereafter, a plurality of stands 4 were put together and inserted in a metal pipe having the outer diameter of 12mm and inner diameter of 9mm, and a multi-filamentary wire having 61 filament was obtained, as shown in Fig. 1. Then, as shown in Fig. 2, the wire was further drawn until it has the diameter of 1.0mm. Referring to Fig. 2, the multi-filamentary wire obtained in this manner consisted of 61 filaments 7 of superconducting material embedded in a matrix 6 of silver.

[0058] Then, referring to Fig. 3, the as-obtained multi-core wires after drawing, which had circular cross section, were twisted to have the twist pitch of 500mm, 100mm, 50mm and 10mm, respectively, and then lightly drawn to the diameter of $0.98\text{mm}\phi$. The wires were rolled to have the tape width of 3.0mm and the thickness of 0.22mm, and heat treatment was effected at 850°C for 50 hours. Thereafter, the wires were further subjected to rolling until it had the thickness of 0.20mm, and further heat treatment at 850°C for 50 hours.

[0059] Fig. 4 is a perspective view showing the oxide superconducting wire of one example of the background of the

present invention obtained in this manner.

[0060] Referring to Fig. 4, the oxide superconducting wire consists of 61 filaments of oxide superconductor in a matrix 2 of silver. The filament 1 is twisted spirally along the longitudinal direction of the wire.

[0061] Fig. 5 is a cross section schematically showing the structure of the oxide superconducting wire shown in Fig. 4. Referring to Fig. 5, the oxide superconducting wire includes filaments 1 of oxide superconductor embedded in a matrix 2 of silver. Matrix 2 serves as a stabilizer.

[0062] In the similar manner, wires having different twist pitches were prepared, and respective wires were cut to have the length of 40mm, critical current density I_c of respective cut wires were measured, and the influence of the twisting on the I_c was studied.

[0063] As a result, critical currents were 21A, 20A, 19A and 17A in the wires having the twist pitches of 500, 100, 50 and 10mm, respectively. Though the critical current decreased slightly as the pitch was made smaller, it was not significantly reduced. The results were when a d.c. current was applied.

[0064] In this manner, four long oxide superconducting wires having the length of 13m and different twist pitches were fabricated, and the obtained wires were wound in the shape of pancakes. The coil had the outer diameter of 100mm ϕ , inner diameter of 40mm ϕ and the height of 6mm. Four coils were fabricated, using superconducting wires having mutually different twist pitches.

[0065] The a.c. loss in the coils obtained in this manner was measured and compared by using an apparatus such as shown in Fig. 10. The method of measurement will be discussed in detail.

[0066] Referring to Fig. 10, by using an a.c. power supply 30, an a.c. current was applied to a coil 31 in liquid nitrogen filled in a cryostat 32. The effective value i_{IN} of the a.c. current was 5A and a frequency f was 50Hz. The coil voltage V_{OUT} and the coil current i_{OUT} generated at both ends of the coil 31 at this time were measured. In order to remove the voltage of inductance and to measure only the resistance component, the coil voltage V_{OUT} was measured in accordance with the 0° phase output voltage of a lock-in amplifier 33. The coil current was measured by using an a.c. voltmeter 34.

[0067] By using the coil current value and the coil voltage value obtained in this manner, the a.c. loss was calculated in accordance with the following equation:

$$\text{a.c. loss} = (\text{coil effective current value}) \times (\text{coil voltage}).$$

[0068] As a result of the measurement, the a.c. loss was 210mW, 170mW, 130mW and 20mW in the wires having the twist pitch of 500, 100, 50 and 10mm, respectively.

[0069] As is apparent from the result, the a.c. loss decreases remarkably as the twist pitch is reduced.

[0070] Meanwhile, a long oxide superconducting wire having the length of 50m was fabricated under the same condition as above except that it was not twisted after drawing. The obtained wire was wound in a double pancake in the similar manner and the a.c. loss was measured in the similar manner, which was 300mW.

[0071] From the above, it can be understood that when a long wire is manufactured, if the wire is twisted after drawing in the steps of drawing and rolling, the a.c. loss of the coil employing the wire, can be significantly reduced.

[0072] The inventors tried to fabricate a wire having the length of 50m and the twist pitch of smaller than 10mm, for example 3mm. However, during the step of twisting, the wire was disconnected at several portions, and such twisting was impossible.

[0073] Therefore, actually, it is necessary to make the twist pitch not smaller than the tape width.

(Embodiment 2 illustrating an example of the present invention)

[0074] Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO were mixed to have the composition ratio of $\text{Bi:Pb:Sr:Ca:Cu}=1.81:0.40:1.98:2.21:3.03$. The mixed powder was successively subjected to heat treatments in an ambient atmosphere at 750°C for 12 hours, 800°C for 8 hours and in a reduced pressure atmosphere of 133.32 Pa (1Torr), at 760°C for 8 hours. At the end of each heat treatment, the powder was pulverized. The powder obtained through such heat treatment and pulverization was further pulverized by a ball mill, and the powder of sub micron order was obtained. The powder was subjected to heat treatment at 800°C for 2 hours, and then filled in a silver pipe having the outer diameter of 12mm and the inner diameter of 11mm.

[0075] Further, a pipe of silver with 10% of gold added having the outer diameter of 12.3mm ϕ and the inner diameter of 12mm ϕ was provided outside the silver pipe.

[0076] The powder filled in the double pipes was drawn to 1mm, and the as-obtained wires were put together and inserted in a silver pipe having the outer diameter of 12mm and the inner diameter of 9mm, to provide a multi-filamentary wire having 61 filaments. This wire was further drawn to have the diameter of 1.0mm.

[0077] The multi-filamentary wires after drawing which had circular cross section were twisted to have the twist pitch

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of 500mm, 100mm, 50mm and 10mm, respectively and lightly drawn to have the diameter of 0.98mm ϕ . The as-obtained wires were rolled to have the thickness of 0.22mm, and then subjected to heat treatment at 850°C for 50 hours.

[0078] Fig. 6 is a cross section showing the structure of the oxide superconducting wire in accordance with this example of the present invention obtained in this manner.

5 [0079] Referring to Fig. 6, the oxide superconducting wire includes filaments 1 of oxide superconductor embedded in a matrix 2 of silver. Around the filament 1, a barrier layer 8 of silver with 10% gold added is provided, surrounding the filament 1.

[0080] In this manner, wires having different twist pitches were fabricated, and the wires were cut to have the length of 400mm. Critical current I_c of each of the wires was measured, and the influence of twisting on the I_c was studied.

10 [0081] As a result, the critical currents were 21A, 20A, 19A and 17A in the wires having the twist pitches of 500, 100, 50 and 10mm, respectively, and I_c was not significantly reduced, though slightly reduced as the pitch was made smaller. The results were when a d.c. current was applied.

15 [0082] Four oxide superconducting multi-filamentary wires having the length of 12m and mutually different twist pitches were fabricated, and the obtained wires were wound in the shape of pancakes. Each coil has the outer diameter of 100mm ϕ , the inner diameter of 40mm ϕ and the height of 6mm. Four coils were fabricated using superconducting wires having mutually different twist pitches.

20 [0083] The a.c. loss of the coils obtained in this manner was measured and compared by using the apparatus such as shown in Fig. 10, as in Example 1. More specifically, a.c. current having the effective value of 5A and frequency of 50Hz was applied to the coil in liquid nitrogen, only the resistance component of the voltage generated at both ends of the coil was detected in accordance with the 0° phase signal of the lock-in amplifier, and the a.c. loss was compared.

25 [0084] As a result, the a.c. loss was 74mW, 40mW, 27mW and 3mW in the wires having the twist pitches of 500, 100, 50 and 10mm, respectively.

[0085] As is apparent from the result, the a.c. loss remarkably reduces as the twist pitch is made smaller.

30 [0086] Meanwhile, a long oxide superconducting wire having the length of 50m was prepared under the same condition as above, except that it was not twisted after drawing and high resistance barrier was not provided. The obtained wire was wound in the shape of a double pancake in the similar manner, and the a.c. loss was measured, which was 300mW.

[0087] From the above, it is understood that when a long wire is manufactured, in the steps of drawing and rolling, if the wire is drawn and then twisted, the a.c. loss of the coil employing the wire can be significantly reduced.

(Example 3 illustrating the background of the present invention)

35 [0088] Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO were mixed to have the composition ratio of $\text{Bi:Pb:Sr:Ca:Cu}=1.81:0.40:1.98:2.21:3.03$. The mixed powder was successively subjected to heat treatments in the ambient atmosphere at 750°C for 12 hours, 800°C for 8 hours and, in a reduced pressure atmosphere of 133.32 Pa (1Torr), at 760°C for 8 hours. At the end of each heat treatment, the powder was pulverized. The powder obtained through the heat treatment and pulverization was further pulverized by a ball mill, and the powder of the sub micron order was obtained. The powder was subjected to heat treatment at 800°C for 2 hours, and then filled in a silver pipe having the outer diameter of 12mm and the inner diameter of 9mm.

40 [0089] The powder filled in the silver pipe was drawn to 1mm, and the as-obtained wires were put together into a silver pipe having the outer diameter of 12mm and the inner diameter of 9mm, to provide a multi-filamentary wire having 61 filaments. The as-obtained wire was further drawn to have the diameter of 1.0mm.

45 [0090] The multi-filamentary wires after drawing were twisted to have the twist pitches of 500mm, 100mm, 50mm and 10mm, respectively, and lightly drawn to have the diameter of 0.98mm ϕ . The resulting wires were rolled to have the tape width of 3.0mm and the thickness of 0.22mm, and then subjected to heat treatment at 850°C for 50 hours. Thereafter, the wires were further drawn to have the thickness of 0.20mm, and subjected to heat treatment at 850°C for 50 hours. Thereafter, the wires having different twist pitches were cut to have the length of 40mm, critical current I_c thereof was measured, and the influence of the twisting on the I_c was studied.

50 [0091] As a result, the critical currents were 21A, 20A, 19A and 17A in the wires having the twist pitches of 500, 100, 50 and 10mm, respectively, and I_c was not significantly reduced, though it was slightly lowered as the pitch was made smaller. The results were when a d.c. current was applied.

[0092] The twist angles of the wires having the twist pitches of 500, 300, 200 and 100mm were studied, which were 0.3°, 0.5°, 0.9° and 1.7°, respectively. By using these tapes, property under strain of the I_c was studied at the bending diameter of 20mm.

55 [0093] The influence of the twist pitch was studied in accordance with the ratio K ($K=I_c/I_{c0}$) of the I_c (I_{c0}) before bending and I_c after bending, the value K was 0.7, 0.85, 0.9 and 0.9 for the twist angle of 0.3°, 0.5°, 0.9° and 1.7°, respectively. It was recognized that the property under strain was improved as the twist angle increased. It was found that the effect was obtained when the angle was made at least 0.5°.

[0094] Four long oxide superconducting multi-filamentary wires having the length of 13m and twist pitches of 500, 100, 50 and 10mm, respectively were fabricated, and the resulting wires were wound in the shape of pancakes. Each coil has the outer diameter of 100mm ϕ , the inner diameter of 40mm ϕ and the height of 6mm. Four coils were fabricated, using superconducting wires having mutually different twist pitches.

5 [0095] The a.c. loss of the coils obtained in this manner was measured and compared by using an apparatus such as shown in Fig. 10, as in Embodiment 1. More specifically, an a.c. current having the effective value of 5A and the frequency of 50Hz was applied to the coil in liquid nitrogen, and only the resistance component of the voltage generated at both ends of the coil was detected in accordance with the 0° phase signal of the lock-in amplifier, and the a.c. loss was compared.

10 [0096] As a result, the a.c. loss of the wires having twist pitches of 500, 100, 50 and 10mm was 190mW, 180mW, 120mW and 10mW, respectively.

[0097] As can be understood from the result, the a.c. loss was reduced remarkably as the twist pitch was made smaller.

15 [0098] A long oxide superconducting wire having the length of 50m was fabricated under the same conditions as above except that it was not twisted after drawing. The resulting wire was wound in a double pancake in the similar manner and the a.c. loss was measured in the similar manner, which was 300mW.

20 [0099] It is understood from the foregoing that when a long wire is manufactured, in the steps of drawing and rolling, if the wire is twisted after drawing, it comes to have superior bending characteristics, less degradation of Ic and the a.c. loss of the coil can be significantly reduced, when the wire is wound into a coil.

(Example 4 illustrating the background of the present invention)

25 [0100] Bi_2O_3 , PbO , SrCO_3 , CaCO_3 and CuO were mixed to have the composition ratio of $\text{Bi}:\text{Pb}:\text{Sr}:\text{Ca}:\text{Cu}=1.81:0.40:1.98:2.21:3.03$. The mixed powder was successively subjected to heat treatments in the ambient atmosphere at 750°C for 12 hours, 800°C for 8 hours and in a reduced pressure atmosphere of 133.32 Pa (1Torr), at 760°C for 8 hours. At the end of each heat treatment, the powder was pulverized. The powder obtained through the heat treatment and pulverization was further pulverized by a ball mill, and the powder of sub micron order was obtained. The powder was heat treated at 800°C for 2 hours, and filled in an alloy pipe of silver to which 10% gold was added, having the outer diameter of 12mm and the inner diameter of 9mm.

30 [0101] The powder filled in the silver alloy pipe was drawn to 1mm, and the as-obtained wires were put together and inserted into an alloy pipe of silver and 10% gold having the outer diameter of 12mm and the inner diameter of 9mm, to provide a multi-filamentary wire having 61 filaments. The wire was further drawn to the diameter of 1.0mm.

35 [0102] The multi-filamentary wires after drawing, which had circular cross section were twisted to have the twist pitches of 500mm, 100mm, 50mm and 10mm, respectively, and lightly drawn to 0.98 ϕ . The as-obtained wires were rolled to have the thickness of 0.22mm and subjected to heat treatment at 850°C for 50 hours. Thereafter, the wires were further rolled to have the thickness of 0.20mm and subjected to heat treatment at 850°C for 50 hours. Thereafter, wires having different twist pitches were cut to have the length of 400mm, the critical current I_c of the wires was measured, and the influence of the twist on the I_c was studied.

40 [0103] As a result, the critical currents were 21A, 20A, 19A and 17A in the wires having twist pitches of 500, 100, 50 and 10mm, and I_c was not significantly reduced, though it was slightly decreased as the pitch was made smaller. The results were when a d.c. current was applied.

45 [0104] In this manner, four long oxide superconducting multi-filamentary wires having the length of 13m and mutually different twist pitches were fabricated, and the resulting wires were wound in the shape of pancakes. Each coil has the outer diameter of 100mm ϕ , the inner diameter of 40mm ϕ and the height of 6mm. Four coils were fabricated using superconducting wires of mutually different twist pitches.

[0105] The a.c. loss of the coils obtained in this manner was measured and compared by using an apparatus such as shown in Fig. 10, as in Example 1. More specifically, an a.c. current having the effective value of 5A and frequency of 50Hz was applied in liquid nitrogen, and only the resistance component of the voltage generated at both ends of the coil was detected in accordance with the 0° phase signal of the lock-in amplifier, and the a.c. loss was compared.

50 [0106] As a result, the a.c. loss was 80mW, 35mW, 33mW and 5mW in the wires having the twist pitches of 500, 100, 50 and 10mm, respectively.

[0107] As is apparent from the results, the a.c. loss was significantly reduced as the twist pitch was reduced.

55 [0108] A long oxide superconducting wire having the length of 50m was fabricated under the same conditions as above except that it was not twisted after drawing. The obtained wire was wound similarly in a double pancake, and the a.c. loss was measured, which was 300mW.

[0109] It is understood from the foregoing that when a long wire is manufactured, in the steps of drawing and rolling, if the wire is twisted after drawing, the a.c. loss of the coil can be significantly reduced when the wire is wound into a coil.

(Example 5 illustrating the background of the present invention)

[0110] By using the tape-like superconducting wire covered by a metal sheath in accordance with the background of the present invention, a small coil having the specification shown in Table 1 below was fabricated and the a.c conduction characteristics was studied in accordance with the conduction conditions specified in Table 2. Silver or silver with 10%Au added thereto was used as the metal sheath. The twist pitch was 20mm and 50mm, and a wire which was not twisted was also fabricated for comparison.

Table 1

Coil Specification		
coil	inner diameter	20mmφ
	outer diameter	40mmφ
	height	12mm
	double pancake	2
tape wire	sheath metal	Ag or Ag+10%Au
	width	2.7mm
	thickness	0.72mm
	length	3m/double pancake

Table 2

Conduction Condition	
frequency	30Hz
applied current	10A
peak magnetic field	±321 gauss
temperature of measurement	77K (in liquid nitrogen)

[0111] The result of measurement of the a.c. loss measured by using the apparatus shown in Fig. 10 as in Example 1 is as shown in Table 3 below.

Table 3

twist pitch	a.c. loss	
	when Ag was used for metal sheath	when Ag+10%Au was used for metal sheath
20mm	100mW	10mW
50mm	150mW	20mW
not twisted	200mW	70mW

[0112] By collecting a plurality of oxide superconducting wires fabricated in the manner as described above, an oxide superconducting cable conductor can be obtained.

[0113] The present invention can be applied not only to the manufacture of a bismuth superconducting wire but also to manufacture of thallium and yttrium superconducting wires.

[0114] Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation.

Claims

- Method of manufacturing an oxide superconducting wire, including the steps of heat treating and then covering with a metal sheath of silver or silver alloy, a powder mainly consisting of an oxide superconducting material,

5 drawing to provide a single-filamentary wire (4) and putting together as-obtained single-filamentary wires (4) to provide a multi-filamentary wire, drawing and rolling, and then heat treating, wherein a silver gold alloy is provided on the surface of the metal sheathed single-filamentary wire (4) or at the interface between said oxide superconducting material and said metal sheath, before the single-filamentary wires (4) are put together to provide said multi-filamentary wire,

10 wherein the resistivity of said silver gold alloy at room temperature is higher than that of the metal sheath, and wherein in the steps of drawing and rolling after said multi-filamentary wire (4) is prepared, after drawing, the as-obtained wire having a circular cross section is twisted.

- 15 2. Method according to claim 1 wherein the silver gold alloy is provided at an interface between said oxide superconducting material and said metal sheath and is silver with 10% gold added.
3. Method to claim 1 or 2, wherein after said wire is twisted, the wire is again drawn and then rolled.
4. Method according to claim 1 or 2, wherein twist pitch after rolling is made to be at least the width of the wire after rolling.
5. Method according to to claim 1 or 2, wherein angle of inclination of the twist after rolling is made at least 0.5° with respect to a direction of said wire.
- 20 6. A tape-like oxide superconducting wire including a plurality of filaments (1) of an oxide superconducting material embedded in a matrix (2), wherein each filament (1) is twisted spirally along the longitudinal direction of said tape-like wire, and wherein a barrier layer (8) of silver gold alloy
 - 25 a) surrounds the filament (1), wherein the resistivity of said silver gold alloy at room temperature is higher than that of the matrix (2) material, or
 - b) is provided on a sheath layer of silver or silver alloy which surrounds the filament (1), wherein, if the sheath layer is of silver alloy, the resistivity of said silver gold alloy at room temperature is higher than that of the sheath layer of silver alloy.
- 30 7. Oxide superconducting wire according to claim 5, wherein said matrix is silver or silver alloy.
8. Oxide superconducting wire according to claim 6 or 7, wherein the barrier layer (8) is provided on a sheath layer of silver or silver alloy which surrounds the filament (1) and is of silver with 10% gold added.
- 35 9. Oxide superconducting wire according to one of the claims 6 to 8, which forms an oxide superconducting coil.
10. Oxide superconducting wire according to one of the claims 6 to 8, which forms an oxide superconducting cable.

40 **Patentansprüche**

- 45 1. Verfahren zum Herstellen eines supraleitenden Oxiddrahtes, das die Schritte des Wärmebehandelns von einem Pulver, das im wesentlichen aus einem supraleitenden Oxidmaterial besteht und des anschließenden Bedeckens von diesem mit einer Metallumhüllung aus Silber oder einer Silberlegierung, des Ziehens zum Vorsehen eines einadrigen Drahtes (4) und des Zusammenbringens der auf diese Weise erhaltenen einadrigen Drähte (4) zum Vorsehen eines mehradrigen Drahtes, des Ziehen und Walzens und des anschließenden Wärmebehandelns aufweist, wobei eine Silber-Gold-Legierung auf der Oberfläche des mit der Metallumhüllung versehenen einadrigen Drahtes (4) oder an der Grenzfläche zwischen dem supraleitenden Oxidmaterial und der Metallumhüllung vorsehen wird, bevor die einadrigen Drähte (4) zusammengebracht werden, um den mehradrigen Draht vorzusehen,
- 50 wobei der spezifische Widerstand der Silber-Gold-Legierung bei Zimmertemperatur höher als der der Metallumhüllung ist, und
- 55 wobei in den Schritten des Ziehens und Walzens nach dem Vorbereiten des mehradrigen Drahtes (4) der auf diese Weise erhaltene Draht mit kreisförmigem Querschnitt nach dem Ziehen verdrillt wird.
2. Verfahren nach Anspruch 1, wobei die Silber-Gold-Legierung an einer Grenzfläche zwischen dem supraleitenden Oxidmaterial und der Metallumhüllung vorgesehen ist und Silber mit hinzugefügten 10 % Gold ist.

3. Verfahren nach Anspruch 1 oder 2, wobei nach dem Verdrillen des Drahtes der Draht erneut gezogen und dann gewalzt wird.
4. Verfahren nach Anspruch 1 oder 2, wobei die Verdrillsteigung nach dem Walzen auf zumindest die Breite des Drahtes nach dem Walzen gebracht wird.
5. Verfahren nach Anspruch 1 oder 2, wobei der Neigungswinkel der Verdrillung nach dem Walzen bezüglich der Richtung des Drahtes zumindest auf 0,5° gebracht wird.
10. 6. Bandartiger supraleitender Oxiddraht mit einer Vielzahl von Adern (1) aus einem supraleitenden Oxidmaterial, die in eine Matrix (2) eingebettet sind, wobei Jede Ader (1) in Längsrichtung des bandartigen Drahtes spiralförmig verdrillt ist, und wobei eine Sperrsicht (8) aus einer Silber-Gold-Legierung
 - 15 a) die Ader (1) umgibt, wobei der spezifische Widerstand der Silber-Gold-Legierung bei Zimmertemperatur höher als der des Materials der Matrix (2) ist, oder b) an einer Umhüllungsschicht aus Silber oder einer Silberlegierung, die die Ader (1) umgibt, vorgesehen ist, wobei dann, wenn die Umhüllungsschicht aus einer Silberlegierung ist, der spezifische Widerstand der Silber-Gold-Legierung bei Zimmertemperatur höher als der der Umhüllungsschicht aus der Silberlegierung ist.
- 20 7. Supraleitender Oxiddraht nach Anspruch 5, wobei die Matrix Silber oder eine Silberlegierung ist.
8. Supraleitender Oxiddraht nach Anspruch 6 oder 7, wobei die Sperrsicht (8) auf einer die Ader (1) umgebenden Umhüllungsschicht aus Silber oder einer Silberlegierung vorgesehen ist und aus Silber mit zugesetzten 10% Gold ist.
- 25 9. Supraleitender Oxiddraht nach einem der Ansprüche 6 bis 8, der eine supraleitende Oxidspule ausbildet.
10. Supraleitender Oxiddraht nach einem der Ansprüche 6 bis 8, der ein supraleitendes Oxidkabel ausbildet.

Revendications

1. Procédé de fabrication d'un fil en oxyde supraconducteur, comprenant les étapes de traitement thermique et ensuite de revêtement par une gaine métallique d'argent ou d'alliage d'argent, d'une poudre constituée principalement d'un oxyde supraconducteur, d'étirage pour obtenir un fil monofilamentaire (4) et de réunion des fils monofilamentaires (4) ainsi obtenus pour constituer un fil à filaments multiples d'étirage et de laminage, et ensuite de traitement thermique, dans lequel un alliage d'argent et d'or est disposé sur la surface un fil monofilamentaire (4) gainé de métal ou à l'interface entre ledit oxyde supraconducteur et ladite gaine métallique, avant que les fils monofilamentaires (4) soient réunis pour constituer ledit fil à filaments multiples, dans lequel la résistivité dudit alliage d'argent et d'or à température ambiante supérieure à celle de la gaine métallique, et dans lequel au cours des étapes d'étirage et de laminage après préparation dudit fil à filaments multiples (4), après étirage, le fil ainsi obtenu de section transversale circulaire est torsadé.
2. Procédé selon la revendication 1, dans lequel l'alliage d'argent et d'or est disposé à une interface entre ledit oxyde supraconducteur et ladite gaine métallique et 10% d'or sont ajoutés à l'argent.
3. Procédé selon la revendication 1 ou 2, dans lequel après torsion dudit fil, le fil est à nouveau étiré et ensuite laminé.
4. Procédé selon la revendication 1 ou 2, dans lequel le pas de torsion après laminage est rendu au moins égal à la largeur du fil après laminage.
5. Procédé selon la revendication 1 ou 2, dans lequel l'angle d'inclinaison de la torsion après laminage est au moins 0,5° par rapport à une direction dudit fil.
- 55 6. Fil en oxyde supraconducteur sous forme de ruban comprenant une pluralité de filaments (1) d'un oxyde supraconducteur noyés dans une matrice (2), dans lequel chaque filament (1) est torsadé hélicoïdalement selon le sens longitudinal dudit fil en forme de ruban et dans lequel une couche d'arrêt (8) d'alliage d'argent et d'or

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- 5 a) entoure le filament (1), dans lequel la résistivité dudit alliage d'argent et d'or à température ambiante est supérieure à celle du matériau de la matrice (2), ou
b) est prévue sur une gaine d'argent ou d'alliage d'argent qui entoure le filament (1), dans lequel, si la gaine est en alliage d'argent, la résistivité dudit alliage d'argent et d'or à température ambiante est supérieure à celle de la gaine d'alliage d'argent.
- 10 7. Fil en oxyde supraconducteur selon la revendication 5, dans lequel ladite matrice est en argent ou en alliage d'argent.
- 15 8. Fil en oxyde supraconducteur selon la revendication 6 ou 7, dans lequel la couche d'arrêt (8) est disposée sur une gaine d'argent ou d'alliage d'argent qui entoure le filament (1) et est en argent avec adjonction de 10% d'or.
- 20 9. Fil en oxyde supraconducteur selon l'une des revendications 6 à 8, qui constitue une bobine en oxyde supraconducteur.
- 25 10. Fil en oxyde supraconducteur selon l'une des revendications 6 à 8, qui forme un câble en oxyde supraconducteur.

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FIG.1

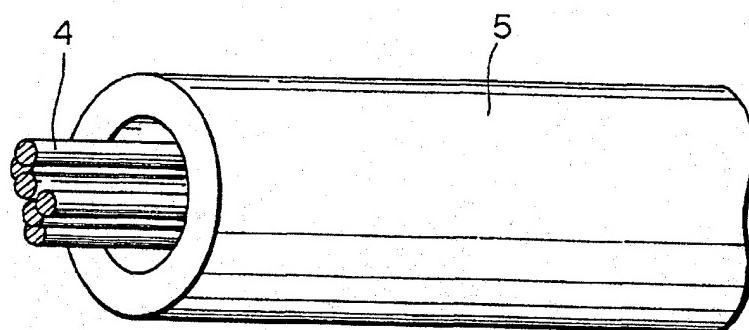


FIG.2

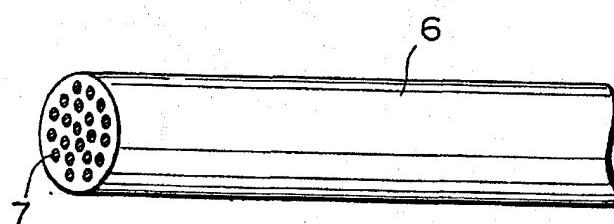


FIG.3

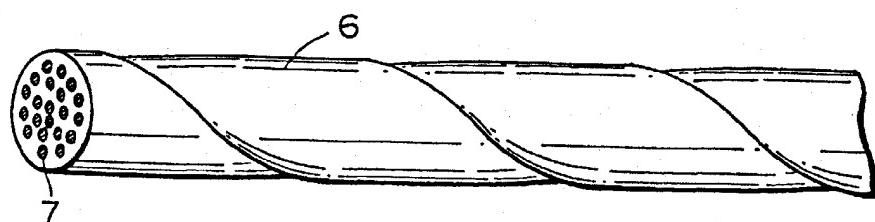


FIG.4

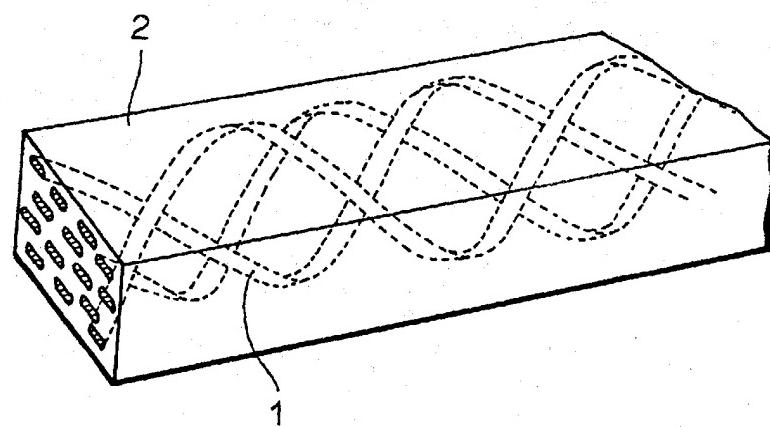


FIG.5

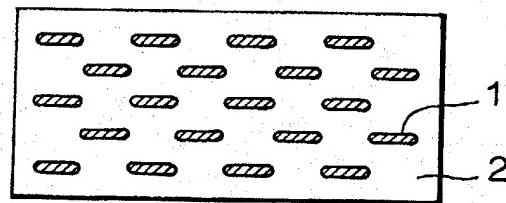


FIG.6

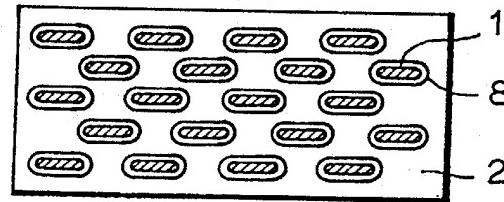


FIG.7

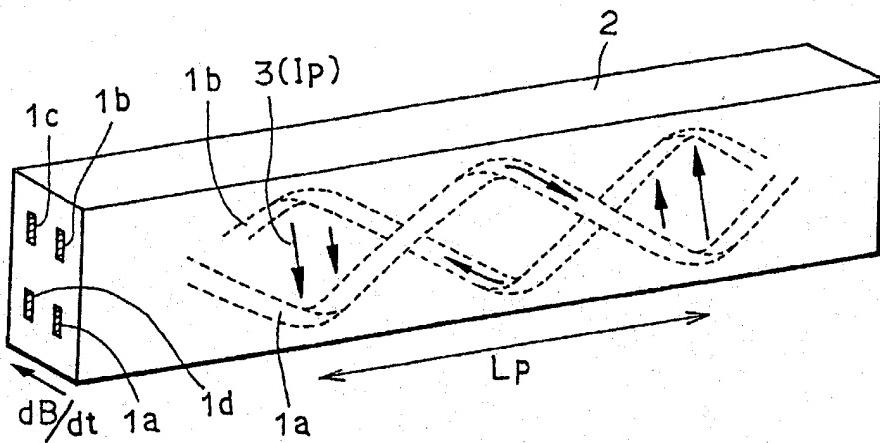


FIG.8

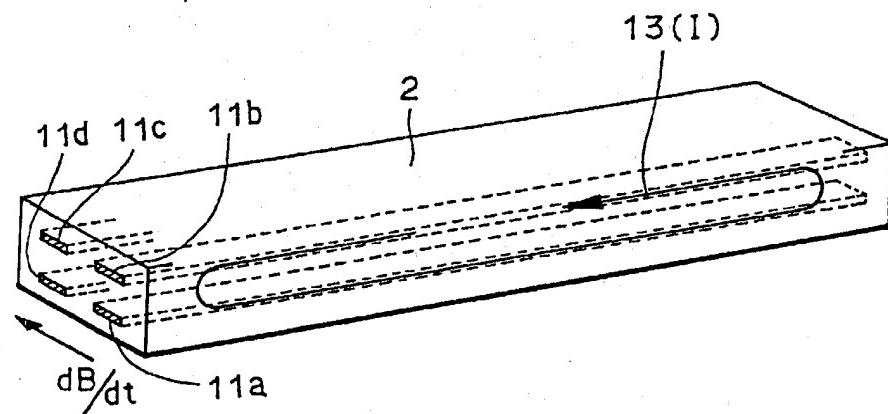


FIG.9

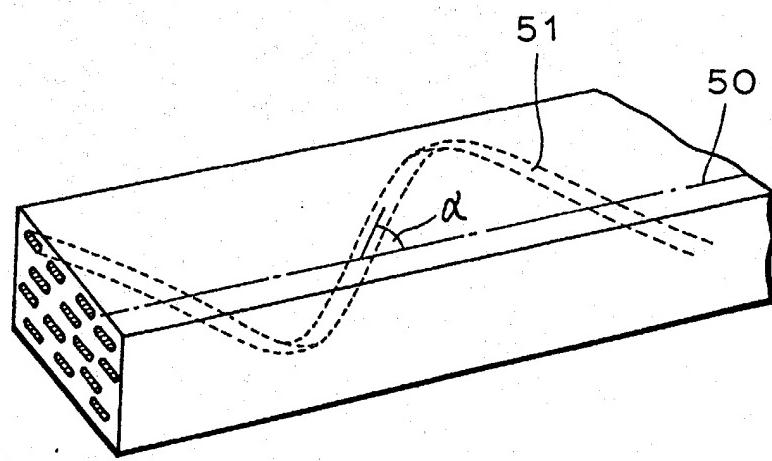


FIG. 10

